

THE MILLIMETER-WAVE SPECTRUM OF METHACROLEIN. TORSION-ROTATION-VIBRATION EFFECTS IN THE EXCITED STATES

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Last year we reported the analysis of the rotational spectrum of *s-trans* conformer of methacrolein $\text{CH}_2=\text{C}(\text{CH}_3)\text{CHO}$ in the ground vibrational state^a. In this talk we report the study of its low lying excited vibrational states. The study is based on room-temperature absorption spectra of methacrolein recorded in the frequency range 150 – 465 GHz using the spectrometer in Lille. The new results include assignment of the first excited torsional state (131 cm^{-1}), and the joint analysis of the $v_t = 0$ and $v_t = 1$ states, that allowed us to improve the model in the frame of Rho-Axis-Method (RAM) Hamiltonian and to remove some strong correlations between parameters. Also we assigned the first excited vibrational state of the skeletal torsion mode (170 cm^{-1}). The inverse sequence of A and E tunneling substates as well as anomalous A-E splittings observed for the rotational lines of $v_{sk} = 1$ state clearly indicate a coupling between methyl torsion and skeletal torsion. However we were able to fit within experimental accuracy the rotational lines of $v_{sk} = 1$ state using the RAM Hamiltonian. Because of the inversion of the A and E tunneling substates the rotational lines of the $v_{sk} = 1$ states were assumed to belong to a virtual first excited torsional state. Finally, we assigned several low- K_a rotational transitions of the excited vibrational states above 200 cm^{-1} but their analysis is complicated by different rotation-vibration interactions. In particular there is an evidence of the Fermi-type resonance between the second excited torsional state and the first excited state of the in-plane skeletal bending mode (265 cm^{-1}).

Support from the French Laboratoire d'Excellence CaPPA (Chemical and Physical Properties of the Atmosphere) through contract ANR-10-LABX-0005 of the Programme d'Investissements d'Avenir is acknowledged.

^aZakharenko O. et al., 69th ISMS, 2014, TI01